NITROGEN as a FRIENDLY ADDITION to STEEL

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ABSTRACT
Interstitial alloying with nitrogen or carbon is a common means of enhancing properties of iron-based alloys. Interstitial nitrogen addition to fcc-phase Fe-Cr-Mn/Ni alloys results in improved mechanical properties, whereas addition of carbon can result in the formation of unwanted carbides. Carbon addition to low alloy, bcc-phase iron alloys significantly improves strength through the formation of carbides, whereas addition of nitrogen in bcc-phase iron alloys can result in porous casting and reduced mechanical properties. This study will show that alloying iron-based alloys with both nitrogen and carbon can produce positive results. Nitrogen addition to Fe-C and Fe-Cr-C alloys, and both nitrogen and nitrogen-carbon additions to Fe-Cr-Mn/Ni alloys altered the microstructure, improved mechanical properties, increased hardness, and reduced wear by stabilizing the fcc-phase and altering (possibly eliminating) precipitate formation.

Key words: nitrogen and carbon interstitials, phase stability, hardness, wear

AIMS and SCOPE

The aim of this study is to extend and build upon the vast amount of research already conducted in nitrogen interstitial alloying of steels, especially stainless steels. In this study the interstitial concentration was expanded to include the combination of both nitrogen and carbon alloy additions. Steel is often defined, or at least often thought of, as iron based alloys containing carbon. This presentation focuses on the addition of nitrogen to a number of different steels (iron-carbon + XX) alloys and the effect that the combination of carbon and nitrogen has on the microstructure and physical properties of these alloys. The data shows, that with certain precautions, the combination of carbon and nitrogen improves the mechanical and wear properties of most steel alloys.

EXPERIMENTATION:

Approximately 250 to 400 grams samples were melted in a high-pressure induction furnace from either elemental stating material, or were remelted commercial alloys (commercial alloys are marked with * in TABLE I). Ingots (25mm diameter by 25mm tall) were furnace cooled. Alloy chemistry, microstructure, hardness (HRA), wear resistance (A), and nitrogen melt pressure are presented in **TABLE I**. The data are for the as-cast material. Matrix phases and precipitates were determined from X-ray diffraction. Wear resistance was determined from abrasive scratch tests, the greater the value of ‘A’ the higher the wear resistance **[REF. 1]**. Limited compression strength data is currently available and presented.

TABLE I

I.D.	Alloy Designation	Composition Cr-Mn-Ni-Ti	Interstitial C - N	Phase	Precipitate	Hardness HRA	Scratch A	σ_{YIELD} MPa	melt N MPa
1	Fe	0-0-0-0	0.004 - 0.03	bcc	(Fe_3C-trace)	26	0.079		0.1
2	Fe - N1		0.004 - 0.75	bcc	Fe_4N	35	0.094		10.0
3	Fe - N2		0.004 - 1.60	bcc	Fe_4N	47	0.169		160.0
4	1008*	0-0.8-0-0	0.015 - 0.03	bcc	Fe_3C	29	0.057		0.1
5	1008* - N1		0.015 - 0.59	bcc	Fe_4N	35	0.149		10.0
6	1045*	0-0.8-0-0	0.43 - 0.04	bcc	Fe_3C	48	0.098	424	0.1
7	1045* - N1		0.43 - 0.50	fcc - bct		67	0.136	498	10.0
8	1080*	0-0.8-0-0	0.78 - 0.05	bcc	Fe_3C	69	0.216	440	0.1
9	1080* - N1		0.78 - 0.45	fcc - bct		70	0.245	609	10.0
10	1080* - N2		0.78 - 1.06	fcc - bct		77	0.357	841	160.0
11	W215	24-0.5-0.4-0	3.1 - 0.04	bct - (fcc)	M_7C_3	76	0.408		0.1
12	W215 - N		3.1 - 0.67	fcc - (bct)	M_7C_3 - Cr_XN_Y	81	0.488		1.0
13	440C*	17-0.6-0.5-0	1.04 - 0.09	bcc	$M_{23}C_6$	66	0.135	817	0.1
14	440C*- N		1.00 - 0.58	fcc	(Cr_2N-trace)	78	0.357	1042	1.0
15	W590	12-1.0-0.2-3.5	1.25 - 0.00	bcc	$M_{23}C_6$ - TiC	65	0.118		0.1
16	W590 - N		1.16 - 0.39	fcc	TiN, (TiC)	75	0.320		1.0
17	W53	8-2.0-6.0-0	3.3 - 0.00	bct - (fcc)	M_7C_3 - Fe_3C	72	0.281		0.1
18	W53 - N		3.2 - 0.67	fcc	M_7C_3	74	0.305		1.0
19	304*	18-1.1-8.2-0	0.09 - 0.05	fcc		45	0.111		0.1
20	304* - N/C		0.20 - 0.71	fcc		55	0.181		1.0
21	316L*	18-2.0-11.8-0	0.03 - 0.10	fcc		50	0.100		0.1
22	JD0	12-2-15-0	0.00 - 0.01	fcc		46	0.142		0.1
23	JD0 - N		0.03 - 0.53	fcc		55	0.219		1.0
24	JD0 - TiC - N1	16-2-15-0.5-0	0.25 - 0.46	fcc		54	0.138		0.1
25	JD0 - TiC - N2		0.11 - 0.62	fcc		58	0.255		1.0
26	NSS086	30- 6-15-0	0.01 - 0.83	fcc		62	0.160	591	0.1
27	NSS084	30-15-15-0	0.01 - 0.84	fcc		60	0.180	565	0.1
28	FeCrMn	15-15-0-0	0.03 - 0.01	fcc - bct		54	0.095	269	0.1
29	FeCrMn - CN1		0.36 - 1.30	fcc		61	0.190	650	1.0
30	FeCrMn - CN2		0.41 - 1.64	fcc		69	0.220	872	10.0

RESULTS and DISCUSSION:

The effects of nitrogen (and carbon) addition will be divided into the three categories of iron-based alloys studied:

(1) **Fe-C,** bcc phase steels,
(2) **Fe-Cr-C,** martensitic phase steels with chrome-carbide precipitates, and
(3) **Fe-Cr-Mn/Ni,** fcc-phase, solid solution stainless steels

Fe - C - N (TABLE I: alloys 1 - 10)

RESULTS:

These Fe-C alloys are the backbone of the steel industry, have the widest range of applications, and are by far the largest quantity of iron-based alloys produced. In this study nitrogen was added to commercial grade steels by high pressure melting. The addition of nitrogen to Fe-C alloys resulted in three different microstructures: (i) for low nitrogen additions, the precipitate formed was Fe_3C and the nitrogen went into the bcc-Fe matrix as interstitial, (ii) for low carbon additions, the precipitate formed was Fe_4N and the carbon went into the bcc-Fe matrix as interstitial, (iii) however for elevated concentrations of both carbon and nitrogen (both above approximately 0.4wt%) the matrix was fcc - bct and no precipitates formed. With increasing nitrogen and/or carbon additions, alloys with each of the three different microstructures increase in hardness (**FIGURE 1**) and wear resistance.

DISCUSSION:

The Fe-C-N alloys described here are unique. Most Fe-C alloys have low nitrogen concentration, generally less than 0.1-2 wt%. These materials retain the bcc lattice matrix and iron-carbide precipitates. The alloys described here are unique in that the nitrogen levels are in excess of 0.5wt%. This high level of nitrogen changed the matrix phase and eliminated formation of precipitates. Stabilizing the fcc matrix increases the alloy's ductility. The elimination of the precipitates resulted in elevated interstitial concentrations that greatly increase an alloy's strength. Thus, these fcc/bct-Fe-C-N alloys have greater strength, (toughness) and abrasive scratch wear resistance than comparable bcc-Fe-C and bcc-Fe_4N alloys.

Details about (i) how to prevent degassing during solidification, (ii) results from an extended range of carbon (0.0 - 1.8 wt%) and nitrogen (0.0 - 1.9 wt%) alloy sample concentrations, and (iii) additional mechanical properties can be found in **[REF. 2, 3]**. Results from these study show that for the 21 precipitation free, fcc, Fe-C-N alloys studied, the hardness (and strength) increases linearly as a function of the total nitrogen + carbon addition (**FIGURE 2**).

Fe - Cr - C - N ALLOYS (TABLE I: alloys 11 - 18)

RESULTS:

Chromium is added to iron-based alloys to enhance the corrosion/oxidation resistance (when in solid solution) and alloyed with carbon to form chrome-carbides so as to increase hardness and improve wear resistance. In this study, four Fe-Cr-C alloys were alloyed with nitrogen. Alloy 440C is bcc and contains 17 wt% chromium and 1 wt% carbon, and alloy W590 that is similar to alloy 440C with part of the chromium replaced with titanium. Alloy W215 is a martensitic, high chromium, high carbon (3wt%) white cast iron. Alloy W53 is also martensitic, high carbon 3wt%, alloyed with both nickel - chromium. (This alloy is often referred to as Nihard 4.) All these alloys are designed for abrasion resistant applications in hostile, corrosive environments.

All four alloys increased hardness and wear resistance with nitrogen addition. For the lower carbon alloys (~1wt% carbon, alloys 440C and W590) nitrogen addition changed the matrix from bcc to fcc, significantly reduced the $M_{23}C_6$ inter-granular precipitate concentration, and formed new intra-granular precipitates predominately nitrides **(FIGURE 3)**. These change resulted in significant improvement in both hardness and abrasion resistance. For the higher carbon alloys (~3 wt%) nitrogen alloying reduced the concentration of Fe_3C precipitate (alloyW215) and formed a second precipitate, Fe_4N (alloy W53) and changed the matrix from a marternsitic phase to fcc-phase. The improvement in hardness and wear resistant for the high carbon alloys were smaller than for the lower carbon alloys, but still significant **(FIGURE 4)**. Preliminary tensile/compression testing shows an increase in yield and ductility when nitrogen is added.

<u>DISCUSSION:</u>
As with the Fe-C alloys discussed above, the alloy with high levels of nitrogen and carbon resulted in a fcc matrix. Nitrogen stabilized the fcc phase, which has an enhanced nitrogen solubility, thereby increasing the alloy's yield strength and hardness. For these Fe-Cr-C/N alloys, there is a direct relationship between hardness and abrasive scratch wear **(FIGURE 5)**. Hardness of each alloy increased by nitrogen alloying.

As with the Fe-C alloys studied above, previous 'high nitrogen' studies of these high chromium, Fe-Cr-C alloys have been restricted to nitrogen levels less than 0.25wt%. In this study nitrogen levels were as high as 0.6wt% resulting in significant difference in microstructure and mechanical properties. The improvement in hardness, yield strength, and wear resistance would suggest that addition of these 'super high nitrogen' levels to Fe-Cr-C alloys is something that is highly desirable in wear applications such as bearings. The nitrogen melt pressures used to produce these alloys are well below those currently available for production of 'high nitrogen' stainless steels (for example: electro-slag remelt operates at 4.2MPa).

Fe - Cr - Mn/Ni - C - N ALLOYS (TABLE I: alloys 19 - 30)
<u>RESULTS:</u>
Stainless steels in this study were fcc-phase alloys stabilized by addition of nickel, manganese, or a combination of nickel and manganese. Nitrogen and/or carbon additions to these alloys can be divided into three groups: (i) no nitrogen or carbon alloys 19, 21, 22, and 28, (ii) nitrogen enhanced alloys, 23, 26, and 27, and (iii) both nitrogen and carbon enhanced alloys 20, 24, 25, 29, and 30. Whereas most commercial stainless steels are designed to be precipitation free and thus have carbon concentrations less than 0.2wt%, in this study precipitation free alloys were obtained with carbon concentrations as high as 0.4wt%, and carbon plus nitrogen concentration in excess of 2wt%. Hardness, yield strength, and abrasive wear resistance increases approximately linearly with increasing nitrogen and/or carbon concentration **(FIGURE 6)**.

DISCUSSION:

Elevated levels of carbon (and nitrogen) addition to these fcc matrixes ‘stainless steel’ alloys did not form precipitates. These results are consistent with the fcc phase Fe-C-N alloys in which, at elevated carbon and nitrogen concentrations, the iron-base alloy matrix was fcc and precipitate free. In contrast to ‘high-nitrogen steels’ these alloys are unique in that, improvement in properties comes not only from high concentrations of nitrogen but also from the addition of high concentrations of both nitrogen and carbon. Yield strength, hardness, and wear resistance increased with increasing interstitial (carbon plus nitrogen) concentration. These results suggest that the two interstitials, nitrogen and carbon, have very similar and equal effects on the matrix.

These high nitrogen- high carbon stainless steel alloys are of significant interest in that the manufacture of these alloys does not require any additional manufacture requirements than that used to prepare high nitrogen steels. Carbon does not significantly reduce the nitrogen solubility and can be added in any form: carbides or elemental carbon.

SUMMARY:

For all the iron-based alloys studied, strength, hardness, and wear resistance improved with increasing nitrogen (and carbon) concentrations.

SEM, X-ray diffraction, Mössbauer, and TEM examination of these high nitrogen and carbon, fcc phase, Fe-C-N and stainless steel showed these alloys to be precipitation free **[REF. 4]**. A recent Mössbauer study of these alloys suggests why the combined higher levels of nitrogen and carbon prevent precipitate formation and stabilize the fcc phase by lowering the fcc to bcc phase transformation temperature.**[REF.5]** Carbon atoms introduce a covalent characteristic to the intermetallic bonds. The nearest-neighbor interstitial carbon atoms aline themselves at 90^{o} with respect to the Fe atom leading to the formation of Fe_3C. In contrast, nitrogen atoms introduce enhanced metallic characteristics to the intermetallic bonds and the nearest neighbor interstitial nitrogen atoms aline themselves at 180^{0} with respect to the Fe atom leading to the formation of Fe_4N. In iron-C-N alloys, nitrogen and carbon have no interstitial nearest neighbors. This suggests that when the combination of nitrogen and carbon are alloyed into the iron-based alloys, both nitrogen and carbon interstitials form a local zone around their nearest iron matrix atoms into which a second interstitial atom (neither nitrogen or carbon) cannot or at least does not easily penetrate, thus reducing precipitate formation. It has also been observed that the contribution of free-electrons at the Fermi surface for these iron-C-N alloys was greater than the sum of the individual contributions, which contributes to stabilizing the fcc-phase.

In iron-based alloys, the fcc-phase matrix has enhanced ductility over bcc phase matrix alloys. The fcc-matrix also has a higher interstitial solubility than does the bcc-matrix. This higher fcc-phase interstitial solubility is further enhanced by the above-mentioned interaction between nitrogen and carbon, greatly increases the strength of these alloys **(FIGURE 7)**. The combination of high strength and enhanced ductility increases the matrix toughness, hardness and wear resistance.

IN CONCLUSION, when properly employed, nitrogen is a friendly addition to steels.

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FIGURES:

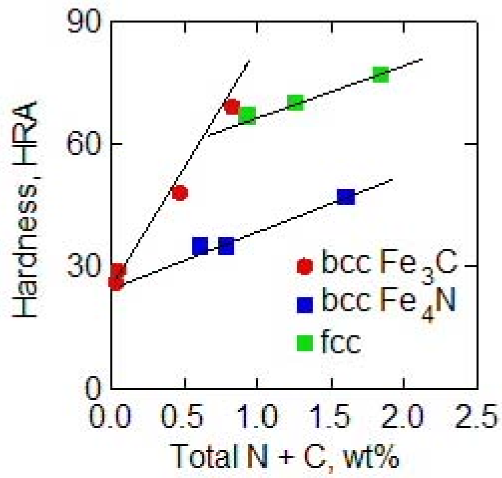


Figure 1: Hardness vs total nitrogen plus carbon. Alloys to which nitrogen has been added to Fe-C alloys could be categorized those that retained the bcc-Fe matrix with Fe_3C precipitates, those that retained the bcc-Fe matrix but formed Fe_4N precipitates, and the high nitrogen high carbon alloys that had no precipitates and had a fcc-matrix.

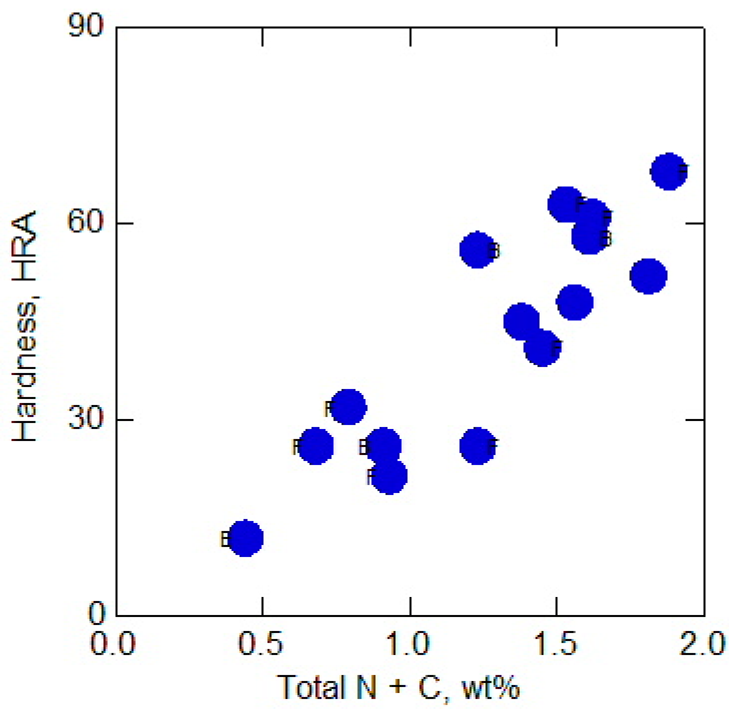


Figure 2: Hardness vs total nitrogen and carbon for fcc precipitation free Fe-C-N alloys (ref. 2 and 3)

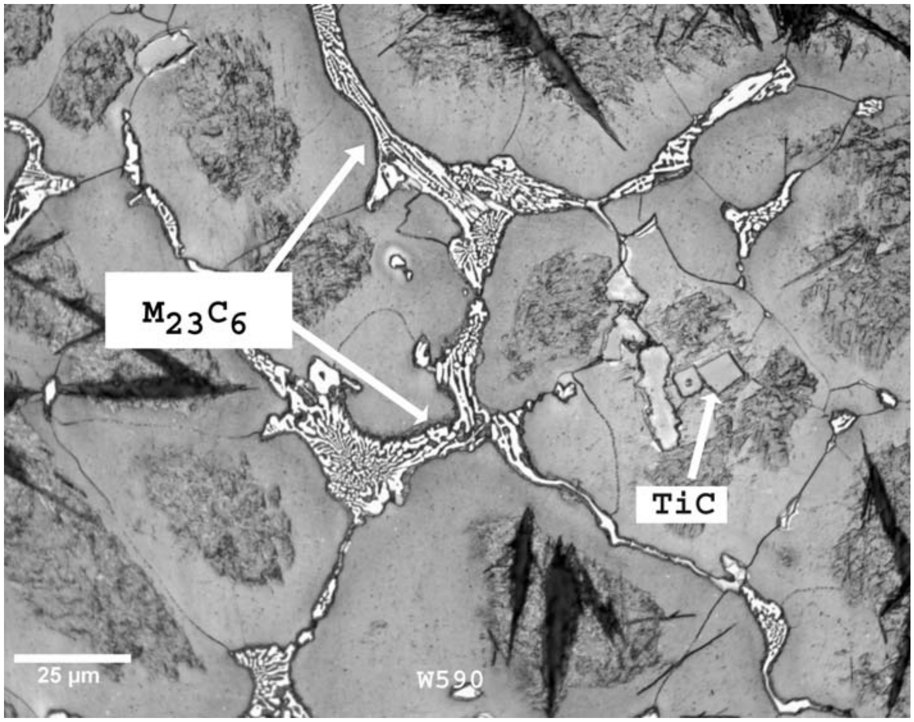
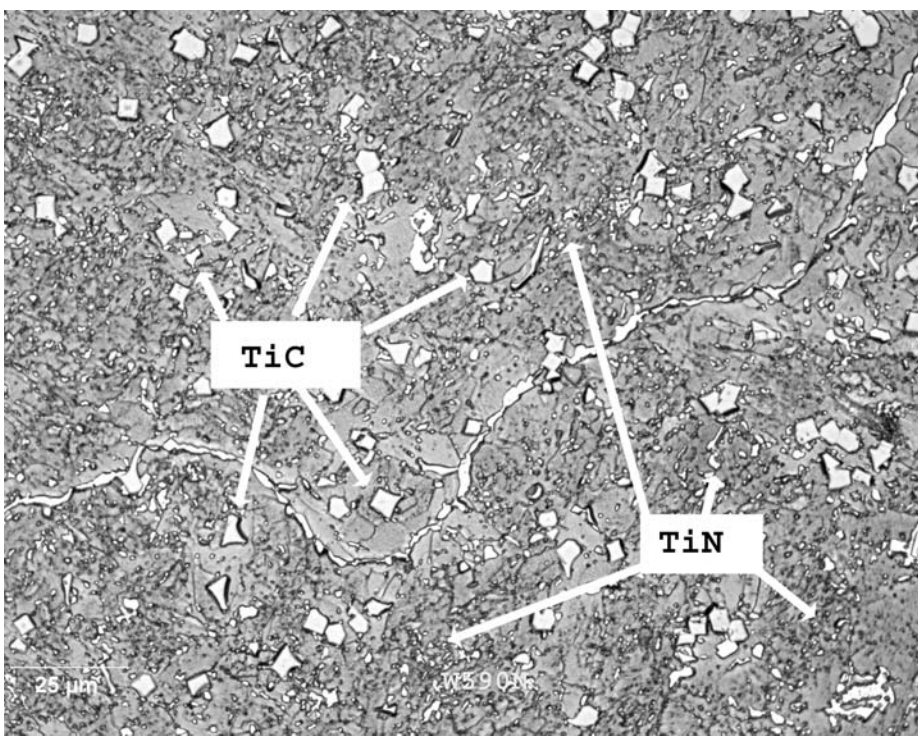


Figure 3 Micrographs of Fe-Cr-C alloy W-590 with and without nitrogen addition.
(a) as-cast structure Alloy 15 without nitrogen, inter-granular iron-carbide precipitates and intra-granular titanium-carbides



(b) as-cast structure Alloy 16 with nitrogen, greatly reduced concentration of inter-granular iron-carbide precipitates, greatly increased concentration of intra-granular titanium-carbides and -nitrides.

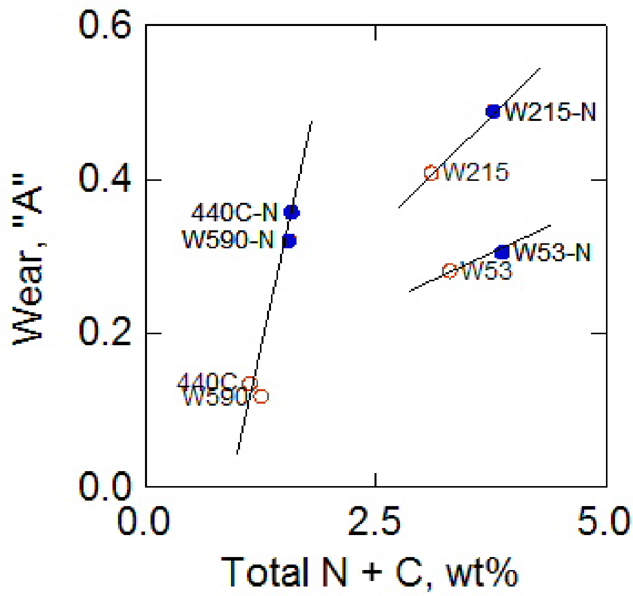


Figure 4: Abrasive scratch wear resistance vs total nitrogen plus carbon for Fe-Cr-C alloys. Increase in wear resistance for all alloys. Greater increase for nitrogen addition to 440C and W590 alloys whose matrix went from bcc to fcc with nitrogen addition. Open circles alloys without nitrogen, filled circles alloys with nitrogen.

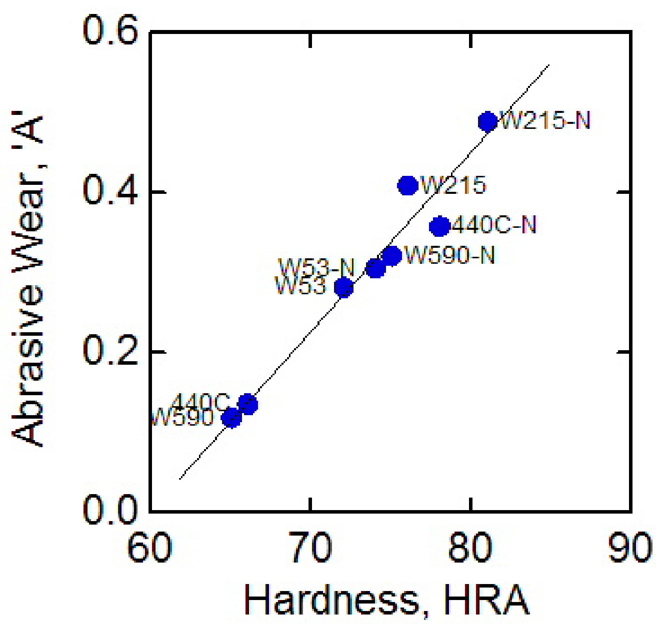


Figure 5: Abrasive scratch wear resistance vs Hardness. Wear resistance increased linearly with increasing hardness for all alloys

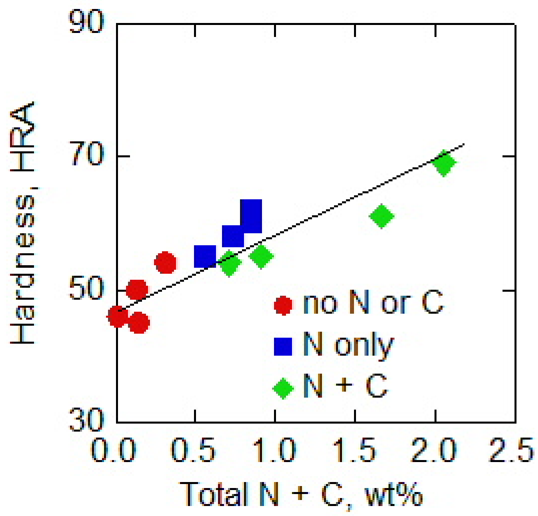


Figure 6: Hardness vs total nitrogen plus carbon. The hardness of these 'stainless steel' alloys increased linearly with increasing interstitial concentration be it nitrogen alone or the combination of nitrogen and carbon.

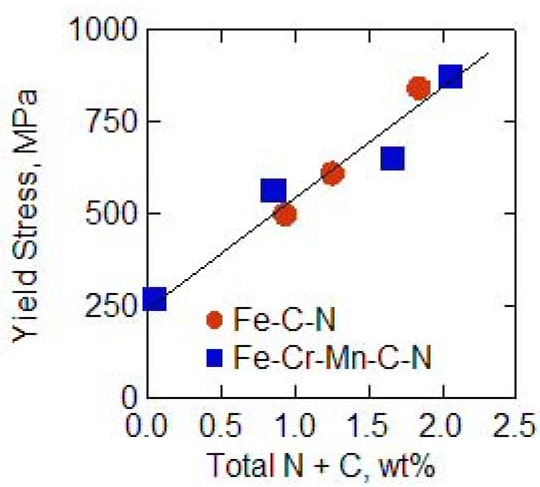


Figure 7: Yield strength vs total nitrogen and carbon. This figure combined the results from the Fe-C-N and the Fe-Cr-Mn/Ni-C-N fcc matrix alloys. Yield strength was a function of the interstitial concentration only.